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ORGANIC METALS AND SEMICONDUCTORS: THE CHEMISTRY OF POLYACETYLENE--ETC(U)
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19. cal doping; donors and acceptors; polyacetylene interfaces

20. ✓ fabricated using $(CH_3)_6$ as the active photoelectrode. ✓ For example, using a sodium polysulfide solution as an electrolyte, $V_{oc} \sim 0.3$ volts and $I_{sc} \sim 40 \mu \text{ amps/cm}^2$ were obtained under an illumination of ca. 1 sun.

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TECHNICAL REPORT NO. 79-8

⁶ Organic Metals and Semiconductors:

The Chemistry of Polyacetylene, (CH)_x, and Its Derivatives.

by

¹⁰ Alan G. MacDiarmid and Alan J. Heeger*

Paper given at

Advanced Study Institute

on the

Physics and Chemistry of Low Dimensional Solids

Tomar, Portugal

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October 21, 1979

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ADVANCED STUDY INSTITUTE ON THE PHYSICS AND CHEMISTRY OF LOW-DIMENSIONAL SOLIDS - TOMAR, PORTUGAL, AUGUST 26-SEPTEMBER 7, 1979

ORGANIC METALS AND SEMICONDUCTORS: THE CHEMISTRY OF POLYACETYLENE, $(CH)_x$, AND ITS DERIVATIVES

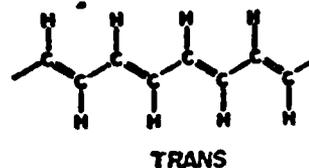
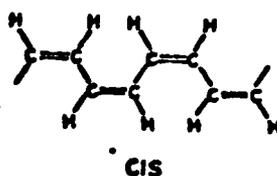
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ABSTRACT

Both cis- and trans-forms of polyacetylene, $(CH)_x$, may be prepared as silvery, flexible, polycrystalline, semiconducting films. The cis-films can be stretched to over three times their original length with partial alignment of the $(CH)_x$ fibrils. Through chemical or electrochemical doping, the electrical conductivity of the films can be increased over twelve orders of magnitude with properties ranging from insulator ($\sigma < 10^{-10} \text{ ohm}^{-1}\text{cm}^{-1}$) to semiconductor to metal ($\sigma > 10^3 \text{ ohm}^{-1}\text{cm}^{-1}$). By the use of donors or acceptors, n-type or p-type polymer, respectively, is produced. Photoelectrochemical photovoltaic cells have been fabricated using $(CH)_x$ as the active photoelectrode. For example, using a sodium polysulfide solution as an electrolyte, $V_{oc} \sim 0.3$ volts and $I_{sc} \sim 40 \mu \text{ amps/cm}^2$ were obtained under an illumination of ca. 1 sun.

Polyacetylene, $(CH)_x$, is the simplest possible conjugated organic polymer and is therefore of special fundamental interest. It can be prepared in the form of lustrous, silvery, flexible, polycrystalline films having any desired cis/trans content by catalytic polymerization of gaseous acetylene, C_2H_2 (1-4):



The cis-rich films can be stretched easily at room temperature in excess of three times their original length with concomitant partial alignment of the $(\text{CH})_x$ fibrils (5,6). Dark red gels of toluene in $(\text{CH})_x$ may be prepared using a lower catalyst concentration (7). Highly porous, very low density, "foam-like" $(\text{CH})_x$ can be obtained from these gels (7). Both cis- and trans- $(\text{CH})_x$ are p-type semiconductors (8) which can be treated with a variety of p- or n-type dopants with concomitant increase in conductivity to give a series of semiconductors and ultimately, "organic metals." This report will be directed primarily towards a description of the more chemically oriented aspects of $(\text{CH})_x$ and its derivatives.

1. DOPING OF $(\text{CH})_x$ FILMS

The various types of dopants and doping procedures, the nature of the $(\text{CH})_x$ chain, and the nature of the dopant in the films will be described below. The terms "cis" and "trans" used in conjunction with a doped film will refer to the principal isomeric composition before doping and does not imply that the isomeric composition either remains constant or changes during the doping process.

1.1. P-type doping

1.1.1. Dopants and methods of doping. When either cis or trans films are exposed to the vapor of electron-attracting substances (p-type dopants) such as Br_2 , I_2 , AsF_5 , H_2SO_4 , HClO_4 , etc. (9,10) they become "doped" with the species and their electrical (11) (Table I) and optical (12) properties change markedly. Dopant

TABLE I
DOPANTS FOR $(\text{CH})_x$ ^{a,b}

	Conductivity (ohm ⁻¹ cm ⁻¹) 25°C
<u>cis</u> - $(\text{CH})_x$	1.7×10^{-9}
<u>trans</u> - $(\text{CH})_x$	4.4×10^{-5}
A. <u>p-type (electron-attracting) dopants</u>	
<u>trans</u> - $[\text{CH}(\text{HBr})_{0.04}]_x$ ^c	7×10^{-4}
<u>trans</u> - $[\text{CHCl}_{0.02}]_x$	1×10^{-4}
<u>trans</u> - $[\text{CHBr}_{0.23}]_x$	4×10^{-1}
<u>cis</u> - $[\text{CH}(\text{ICl})_{0.14}]_x$	5×10^1
<u>cis</u> - $[\text{CHI}_{0.30}]_x$	5.5×10^2

(continued on next page)

TABLE I (continued)

<u>trans</u> -[CH _{1.0} I _{0.20}] _x	1.6 x 10 ²
<u>cis</u> -[CH(I ₂) _{0.15}] _x	4.0 x 10 ²
<u>trans</u> -[CH(AsF ₅) _{0.10}] _x ^c	4.0 x 10 ²
<u>cis</u> -[CH(AsF ₅) _{0.10}] _x	1.2 x 10 ³
<u>cis</u> -[CH _{1.1} (AsF ₆) _{0.10}] _x	ca. 7 x 10 ²
<u>cis</u> -[CH(SbF ₆) _{0.05}] _x	4.0 x 10 ²
<u>cis</u> -[CH(SbCl ₆) _{0.009}] _x	1 x 10 ⁻¹
<u>cis</u> -[CH(SbCl ₈) _{0.0095}] _x	1 x 10 ¹
<u>cis</u> -[CH(SbCl ₅) _{0.022}] _x	2
<u>cis</u> -[CH(BF ₂) _{0.09}] _x ^d	1 x 10 ²
<u>cis</u> -[CH(SO ₃ F) _y] _x	7 x 10 ²
<u>cis</u> -[CH(ClO ₄) _{0.0645}] _x	9.7 x 10 ²
<u>cis</u> -[CH(AsF ₄) _{0.077}] _x	2.0 x 10 ²
<u>cis</u> -[CH _{1.011} (AsF ₅ OH) _{0.011}] _x ^e	ca. 7 x 10 ²
<u>cis</u> -[CH _{1.058} (PF ₅ OH) _{0.058}] _x ^e	ca. 3 x 10 ¹
<u>cis</u> -[CH(H ₂ SO ₄) _{0.106} (H ₂ O) _{0.070}] _x	1.2 x 10 ³
<u>cis</u> -[CH(HClO ₄) _{0.127} (H ₂ O) _{0.297}] _x	1.2 x 10 ³

B. n-type (electron-donating) dopants^c

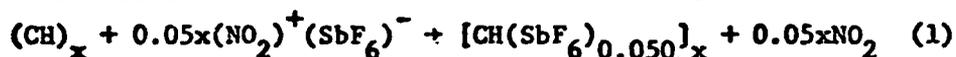
<u>cis</u> -[Li _{0.30} (CH)] _x	2.0 x 10 ²
<u>cis</u> -[Na _{0.21} (CH)] _x	2.5 x 10 ¹
<u>cis</u> -[K _{0.16} (CH)] _x	5.0 x 10 ¹
<u>trans</u> -[Na _{0.28} (CH)] _x	8.0 x 10 ¹

- "cis" or "trans" refers to the principal isomeric composition before doping
- composition by elemental analysis except where stated otherwise
- composition by weight uptake
- dopant used: (SO₃F)₂. No composition or analysis given. Anderson, L.R., Pez, G.P., and Hsu, S.L.: 1978, J.C.S. Chem. Comm., pp.1066.
- by electrochemical doping using [(n-C₄H₉)₄N]⁺[PF₆]⁻. Nigrey, P.J., MacDiarmid, A.G., and Heeger, A.J.: 1979, unpublished observations.

pressures <1 torr are usually satisfactory. With many dopants the conductivity increases rapidly through the semiconducting regime to the metallic regime. The concentrations of the dopants given

in Table I are generally the maximum or close to the maximum value readily obtainable. Doping can be terminated at any degree of lower doping level desired, with corresponding lower conductivity.

Salts containing the $(\text{NO})^+$ or $(\text{NO}_2)^+$ ions also act as good dopants (10). For example, the SbF_6^- group can be introduced readily into $(\text{CH})_x$ simply by treating a $(\text{CH})_x$ film (ca. 85% cis isomer) with a $\text{CH}_3\text{NO}_2\text{-CH}_2\text{Cl}_2$ solution of the appropriate salt. Thus, $(\text{NO}_2)^+(\text{SbF}_6)^-$ yields golden, flexible, highly conducting films of $[\text{CH}(\text{SbF}_6)_{0.05}]_x$ (Table I) with liberation of NO_2 , viz.,

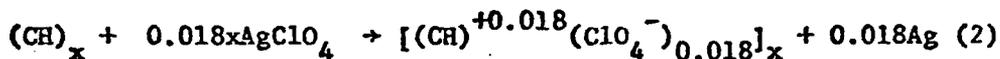


It has been found very recently that $(\text{CH})_x$ films may be doped electrochemically either to the semiconducting or metallic regime (13). This is a most important development since it opens up a general, very simple, readily controllable means of doping with a wide variety of species which can not be introduced by any obvious conventional chemical means. For example, it was found that when a strip of $(\text{CH})_x$ film (ca. 82% cis-isomer) was used as the anode in the electrolysis of aqueous 0.5M KI solution with a potential of 9 V. it was doped during ca. 0.5 hour to the metallic state, to give, by elemental analysis, $(\text{CHI}_{0.07})_x$. It is important to note that the flexible, golden-silvery films contained no oxygen (total C, H, and I content=99.8%) and hence had undergone no hydrolysis and/or oxidation during the electrolytic doping process. When the $(\text{CH})_x$ was used as the anode in the electrolysis of 0.5M $[(n\text{-C}_4\text{H}_9)_4\text{N}]^+[\text{ClO}_4]^-$ in CH_2Cl_2 at 9 V., doping occurred during ca. 1 hour to give highly conducting (Table I), flexible films which, by elemental analysis, had the composition $[\text{CH}(\text{ClO}_4)_{0.0645}]_x$ (13). Lower doping levels obtained during shorter electrolysis times gave material having conductivities in the semiconductor region. Similar results were obtained by the electrolysis of methylene chloride solutions of $[(n\text{-C}_4\text{H}_9)_4\text{N}]^+[\text{SO}_3\text{CF}_3]^-$ and $[(n\text{-C}_3\text{H}_7)_3\text{NH}]^+[\text{AsF}_6]^-$ both of which gave highly conducting golden-silvery flexible films. The former is assumed to contain the (SO_3CF_3) and the latter, the (AsF_4) species, since elemental analysis of the film gave a composition corresponding to $[\text{CH}(\text{AsF}_4)_{0.077}]_x$. The (AsF_4) is probably formed by a reaction sequence involving proton abstraction from $[(n\text{-C}_3\text{H}_7)_3\text{NH}]^+$ by fluorine atoms from AsF_6^- during the electrolysis process (13).

1.1.2. Nature of the $(\text{CH})_x$ chains and dopant species. Raman studies show that the iodinated and brominated films should be formulated as $[(\text{CH})^+y(\text{X}_3)^-y]_x$ where $\text{X}=\text{Br}$ or I , at least a significant portion of the halogen being present as the X_3^- ion (14). The halogen partly depopulates the pi bonding system and oxidizes the $(\text{CH})_x$ to a polycarbonium ion chain. This conclusion is supported by carbon 1s core shifts from ESCA studies (15). The $(\text{NO})^+$ ions are also excellent species for oxidizing the pi system of $(\text{CH})_x$

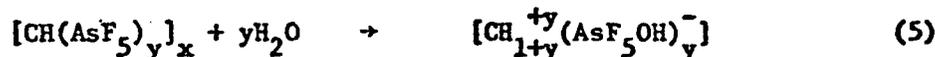
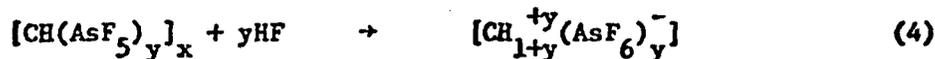
and are capable of concomitantly introducing anions which stabilize the polycarbonium ion chains (10). For example, the $[\text{CH}(\text{SbF}_6)_{0.050}]_x$ species given in equation 1 is more appropriately formulated as $[\text{CH}^{+0.050}(\text{SbF}_6)^{-0.050}]_x$.

The most simple and general method for simultaneously oxidizing the $(\text{CH})_x$ pi system and introducing stabilizing anions appears to be that involving electrochemical doping (13). Thus, species such as $[\text{CH}(\text{ClO}_4)_{0.0645}]_x$, $[\text{CH}(\text{AsF}_4)_{0.077}]_x$, etc. formed electrochemically as described in Section 1.1.1. are believed to contain the $(\text{ClO}_4)^-$ and $(\text{AsF}_4)^-$ ions, respectively, although the extent to which charge transfer to the anionic species occurs may be expected to vary according to the nature of the dopant. It is interesting to note that AgClO_4 has also been found to dope $(\text{CH})_x$ films with $(\text{ClO}_4)^-$ ion, although to lower conductivity levels (16) (ca. $3 \text{ ohm}^{-1}\text{cm}^{-1}$) than that obtained with electrochemical doping. The resulting film is contaminated with metallic silver. In this case, the Ag^+ ion acts as the oxidizing agent, viz.,



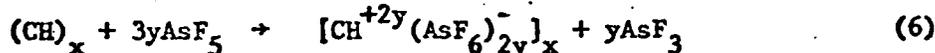
Although most studies of $(\text{CH})_x$ have been carried out on AsF_5^- or I_2 -doped films, the actual chemical form in which the AsF_5^- exists in the film is still not completely clear. When $(\text{CH})_x$ film is treated with very pure AsF_5 vapor in a vacuum line pre-treated with AsF_5 , elemental analyses for C, H, As and F give an arsenic to fluorine ratio of 1:5 (Table I) (17, 18). The sum of the elemental analyses is 99.7% or better and hence the film contains no significant amounts of oxygen. Photoelectron spectroscopy also shows the principal arsenic species contains arsenic and fluorine in the ratio of 1:5 (15). Since epr (19) and magnetic susceptibility studies (20) show the paramagnetic radical anion, $\text{AsF}_5^{\cdot -}$ is not present it seems that the AsF_5^- might be in the form of the previously unreported diamagnetic $(\text{As}_2\text{F}_{10})^{-2}$ ion. If the $[\text{CH}(\text{AsF}_5)_y]_x$ film is treated either with AsF_5 vapor containing HF or is immersed in 42% aqueous HF, then elemental analyses for C, H, As and F give an arsenic to fluorine ratio of 1:6 (Table I) (17). Again, the sum of the elemental analyses for all elements is greater than 99.7%. If, on the other hand, the $[\text{CH}(\text{AsF}_5)_y]_x$ film is pumped for many hours in a vacuum system containing possible traces of air, elemental analyses corresponding to $[\text{CH}_{1+y}(\text{AsF}_5\text{OH})_y]_x$, (Table I), are obtained. In this respect, it might be noted that many salts containing the $[\text{AsF}_5(\text{OH})]^-$ ion are known. The conductivity of all three types of species is essentially identical. These experimental observations are consistent with the reactions below:





The weak protonic acids, HF and HOH can be regarded as combining with the AsF_5 species to give the strong protonic acids, " $\text{H}^+(\text{AsF}_6)^-$ " and " $\text{H}^+(\text{AsF}_5\text{OH})^-$ ", respectively, which then dope the $(\text{CH})_x$ portion of the material according to equations (4) and (5) (17):

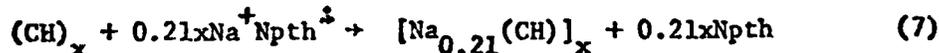
Other investigators have shown on the basis of X-ray absorption and infrared data that AsF_5 -doped film, of unknown elemental composition, contains the AsF_6^- ion (21). This is in no way inconsistent with the above conclusions based on elemental analyses; indeed, it supports the formulation of the $[\text{CH}_{1+y}^{+y}(\text{AsF}_6)^-]_x$ species given above. However, these investigators suggest that the $(\text{AsF}_6)^-$ ion arises through the reaction below which involves disproportionation of the AsF_5 :



Since AsF_3 is readily removed by pumping (21), the resulting material should always contain arsenic to fluorine in the ratio of 1:6. This is in conflict with the elemental analytical data for the $[\text{CH}(\text{AsF}_5)_y]_x$ material. Since $[\text{CH}(\text{AsF}_5)_y]_x$ decomposes thermally with the liberation of gaseous HF and $y\text{AsF}_3$, it is also quite possible that $[\text{CH}(\text{AsF}_5)_y]_x$ could be converted to $[\text{CH}_{1+y}^{+y}(\text{AsF}_6)^-]_x$ according to equation (4) by the HF so formed under certain conditions of handling or storage of the AsF_5 -doped films.

1.2. N-type doping

Electron-donating, i.e. "n-type" dopants, may also be introduced into $(\text{CH})_x$ films (22) (Table I) simply by immersing the film in a THF solution of e.g. sodium naphthalide, viz.,



A very large increase in conductivity is noted but it is not as great as that observed with most p-type dopants. Alkali metals may also be introduced by, for example, allowing a liquid sodium/potassium alloy at room temperature, or molten potassium to contact a $(\text{CH})_x$ film (23). A liquid sodium amalgam will also Na-dope the film at room temperature (23). Preliminary experiments indicate that the $(\text{CH})_x$ pi system may also be reduced electrochemically to give n-type doping by, for example, the electrolysis of a solution of LiI in THF using a $(\text{CH})_x$ film as the cathode, to give $[\text{Li}_y^+(\text{CH})^{-y}]_x$ films (13).

The $(\text{CH})_x$ chain in these materials may be considered as a polycarbanion associated with the corresponding M^+ metal ion. They are extremely sensitive to air and moisture. This appears to be a direct result of the anionic nature of the $(\text{CH})_x$ chain and is not directly related to the presence of the metal ion. Thus it seems likely that all n-doped $(\text{CH})_x$ will be highly reactive regardless of the attendant metal ion, which of course is stable to air and water. Treatment of Na-doped $(\text{CH})_x$ with D_2O results in partial hydrogenation of the carbon-carbon double bonds (17).

2. PHOTOELECTROCHEMICAL REACTIONS AT POLYACETYLENE INTERFACES

A chemical reaction involving a reduction process, e.g.,

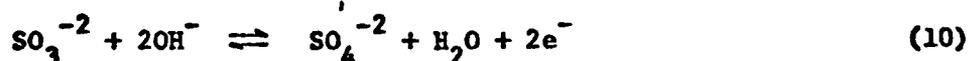


can take place with the concomitant production of an electric current when a p-type $(\text{CH})_x$ film, immersed in a solution containing the oxidized and reduced forms of an appropriate couple, is irradiated with light of appropriate wavelength (24). In the case of the polysulfide system, the reverse (oxidation) process,



will take place simultaneously at the counter electrode, e.g., Pt, which is not irradiated. The ions produced at a given electrode then diffuse to the other electrode and become available for reuse at that electrode as shown in Figure 1. The process is, therefore, continuous as long as the $(\text{CH})_x$ electrode is irradiated with light of appropriate wavelength (24,25). A definite photovoltaic effect can be observed ($V_{oc} \sim 0.3$ volts under illumination of ca. 1 sun) even with the simple oc set-up shown in Figure 1 if a fairly thick film of trans- $(\text{CH})_x$ is used in order to reduce somewhat the otherwise high resistance of the $(\text{CH})_x$ electrode. By using a different cell configuration, described in detail elsewhere (24,25), an open circuit current of ca. $40 \mu\text{ amps/cm}^2$ may be obtained. This will undoubtedly be increased by using partially doped $(\text{CH})_x$ and thinner films. Since $(\text{CH})_x$ is a p-type semiconductor, photo-generated electron-hole pairs become separated at the $(\text{CH})_x$ -electrolyte interface and electrons are injected into the electrolyte as shown in Figure 2.

Preliminary experiments have been carried out (24) using aqueous solutions of the couple



with qualitatively similar results. It therefore seems highly likely that it should be possible to fabricate a variety of photo-

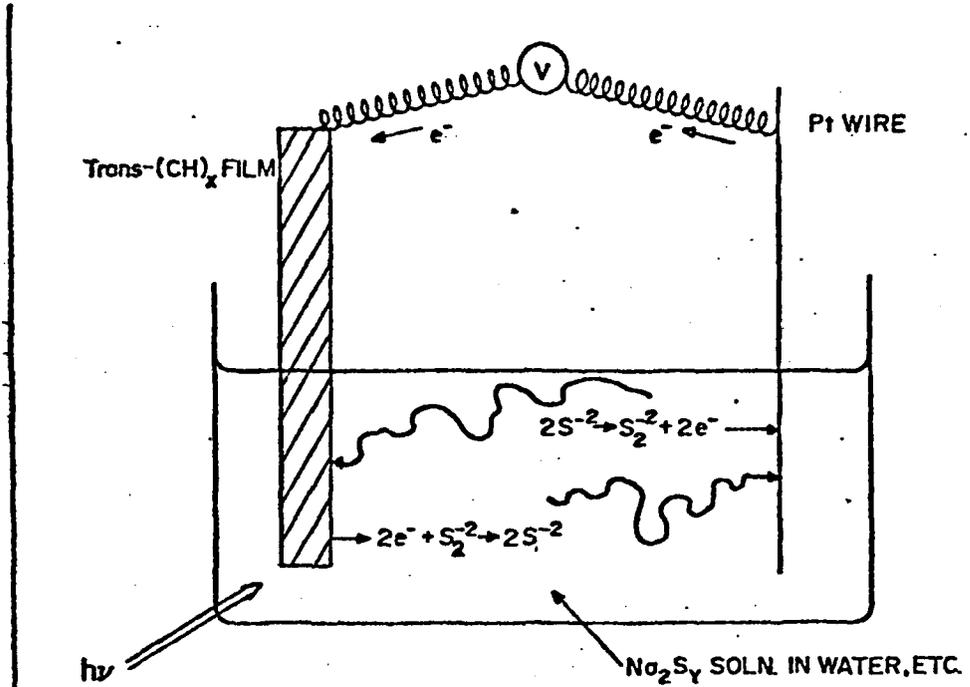


Figure 1. Simple (CH)_x/sodium polysulfide photoelectrochemical cell.

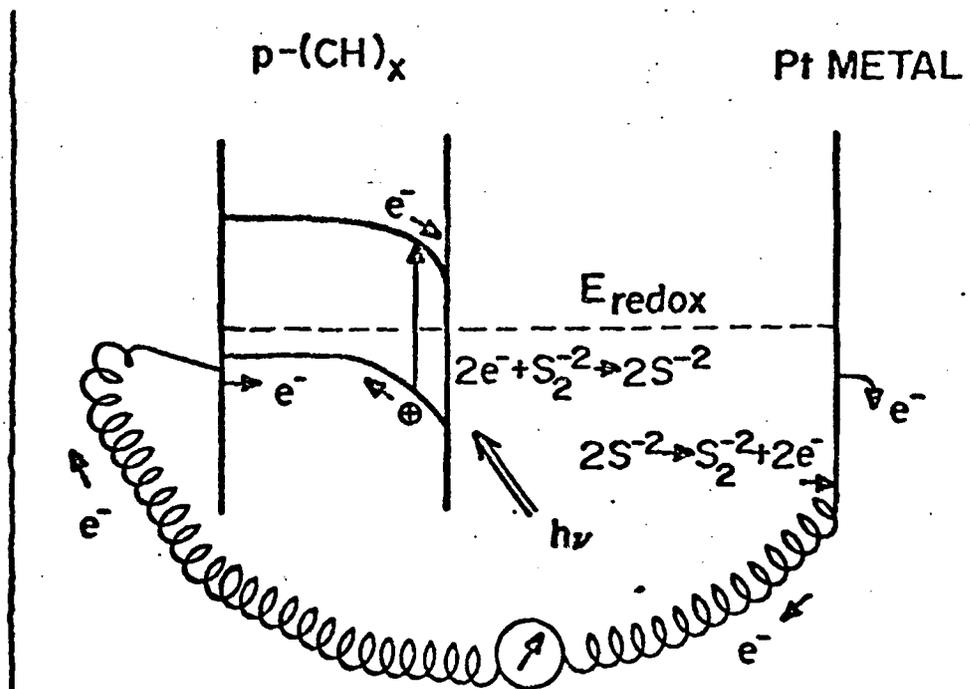


Figure 2. Electrode processes in a (CH)_x/sodium polysulfide photoelectrochemical cell.

voltaic cells using $(\text{CH})_x$ electrodes immersed in aqueous or non-aqueous solutions of appropriate redox couples.

3. CONCLUSIONS

It can be seen clearly that $(\text{CH})_x$ is quite remarkable in that its conductivity can be readily modified to span an extraordinarily large range. Considering possible polyacetylene derivatives, replacement of some or all of the hydrogen atoms in $(\text{CH})_x$ with organic or inorganic groups, copolymerization of acetylene with other acetylenes or olefins, and the use of different dopants should lead to the development of a large new class of conducting organic polymers with electrical properties that can be controlled over the full range from insulator to semiconductor to metal. Furthermore, there is considerable potential for the possible application of parent or doped $(\text{CH})_x$ to the fabrication of various types of electronic devices, solar cells, etc.

4. ACKNOWLEDGMENT

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July 18, 1980

TO WHOM IT MAY CONCERN:

I wish to inform you that ONR report # 79-8 had an incorrect manuscript attached to it. Enclosed is report # 79-8 with the correct manuscript. We apologize for any inconvenience that it may have caused.

Sincerely yours,

Joann Miliken
Joann Miliken

JM/grm
enclosure

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